Kinetic Study of Desulfurization and Deoxidation of Ferroalloys in Vacuum Melting

Kinetic Study of Desulfurization and Deoxidation of Ferroalloys in Vacuum Melting*

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Synopsis

The vacuum melting of Fe-O, Fe-S, Fe-C, Fe-C-S and Fe-Si-S alloys was carried out at 1600°C, by using a high frequency induction furnace and the rate of desulfurization was examined by applying Langmuir's equation and an equation based upon Fick's first law. The rate of deoxidation was also investigated. The effect of sulfur on the deoxidation of Fe-C alloys was considered from the change in the surface tension of iron melt due to the presence of sulfur.

I. Introduction

The desulfurization of Fe-S, Fe-C-S, Fe-Si-S and Fe-C-Si-S alloys in vacuum melting has been considered from the standpoint of chemical equilibrium.[1] However, the experiment of Fe-S alloy system, which was necessary for the consideration of the other alloy systems, was few, and since oxygen analysis was not made, the effect of oxygen on desulfurization was obscure. Furthermore, it was required to investigate the desulfurization from a kinetic point of view. Such being the case, the present work was carried out.

II. Experimental procedure

Fe-O, Fe-S, Fe-Si-S, Fe-C and Fe-C-S alloys were synthesized in atmosphere from electrolytic iron, metallic silicon, graphite and iron sulfide. The chemical composition in percentage of the electrolytic iron was 0.005 C, 0.007 Si, 0.006 S, 0.004 Al, 0.010 Mn, 0.004 N and trace of P, and that of the metallic silicon was 98.81 Si, 0.56 Fe, 0.17 Al and 0.26 Ca. The graphite contained less than 0.1 per cent ash.

These alloys were melted in vacuum at 1600°C for 5 to 90 minutes and then cast into 10 mm ϕ iron mold in vacuum or in argon at 1 atm. pressure. Melting amount was 100 to 200 g, and according to circumstances alumina, magnesia and graphite crucibles were used. The typical analytical results of compositions of these crucibles were as follows: In the case of the alumina crucible, silica and sulfur were 0.94 per cent and 0.03 per cent, respectively and in the case of the

* The 1099th report of the Research Institute for Iron, Steel and Other Metals.

(1) R. Ohno, Sci. Rep. RITU, **A 12** (1960), 353.

magnesia crucible, silicon and sulfur were 1.6 per cent and 0.004 per cent, respectively. The graphite crucibles were shaped from graphite rod containing less than 0.1 per cent ash, the size being 28 mm in internal diameter, 38 mm in external diameter and 100 mm in height.

For vacuum melting, the same high frequency induction furnace that was used in the previous experiment[1] was used. The temperature of melt was measured by an optical pyrometer. Vacuum pressure during vacuum melting was $10^{-3} \sim 10^{-4}$ mm Hg.

Sulfur in metal samples was determined by the combustion volumetric method, and oxygen by the vacuum fusion method or by the inert gas fusion method.

III. Experimental results and considerations

1. Fe-O system

Experimental results are shown in Table 1. Two hundred grams of each of original alloys was heated in vacuum from room temperature. The time at 1600°C was shown in Table 1. Casting was made in vacuum. In the case of an original alloy containing 0.2 per cent O, oxygen decreased to 0.1 per cent. This original alloy was prepared by melting electrolytic iron in atmosphere. When electrolytic iron was used as an original alloy, the deoxidation did not occur. The same might be said of the melting in magnesia crucibles because the same electrolytic iron was used. In Table 1 is shown the original oxygen content in the electrolytic iron which was heated to 1600°C in an alumina crucible in argon at 1 atm. pressure and then cast into the iron mold.

Table 1. Variation of carbon and oxygen contents during vacuum melting.

Crucible		Original alloy	Time of vacuum melting (min)				
			15	30	45	60	90
Alumina	%C	0.008	0.005	0.005	0.005	0.006	—
	%O	0.20	0.11	0.10	0.10	0.10	—
Alumina	%C	0.005	0.005	0.005	0.005	0.004	0.003
	%O	0.06	0.063	0.063	0.061	0.072	0.069
Magnesia	%C	—	0.007	0.003	0.003	0.002	0.016
	%O	—	0.040	0.063	0.063	0.066	0.067

The deoxidation of Fe-O alloy containing 0.2 per cent O cannot be explained from the change in its carbon content according to stoichiometric relations in the following reactions:

$$\underline{C} + \underline{O} = CO\,(g) \tag{1}$$

and

$$\underline{C} + 2\underline{O} = CO_2\,(g)\,, \tag{2}$$

where the underscore and (g) refer to components dissolved in the alloy and in the

gaseous state, respectively. Therefore, the following reactions are proposed:

$$\underline{O} = \frac{1}{2} O_2 (g) \tag{3}$$

and

$$\underline{O} = O (g) \tag{4}$$

However, P_{O_2} and P_O, the equilibrium partial pressures respectively of O_2 and O in the reactions (3) and (4) calculated from the standard free energy changes[2][3] of the reactions (3) and (4) are very low, that is, $P_{O_2}=9.2\times10^{-9}$ atm[4] and $P_O=2.3\times10^{-8}$ atm in 0.23 per cent O (saturation) at 1600°C.

According to L. Brewer and G.M. Rosenblatt[5], in the first period of transition metals from scandium to nickel, major vaporizing oxide species is M O molecule in every instance except nickel, and for iron at low oxygen concentration

$$R = (O/M)_{vapor}/(O/M)_{metal} = 10^{0.4},$$

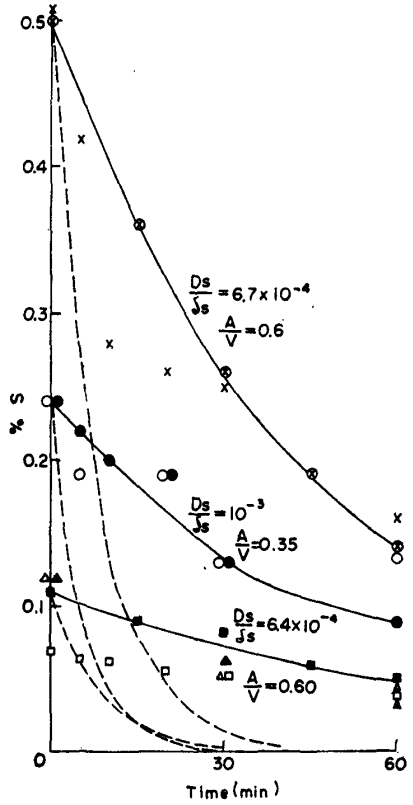
where (O/M) *vapor* is the atomic ratio of oxygen to metal in vapor and (O/M) *metal* is defined as the ratio of mole fraction of oxygen to mole fraction of metal. This value shows a possibility of deoxidation of Fe-O alloy system in vacuum melting. A further investigation is required for the deoxidation reaction in this system.

2. Fe-S system

Experimental results are shown in Figs. 1 and 2 and in Table 2. The marks in Figs. 1 and 2 correspond with each other. Vacuum melting was made after heating to 1600°C in argon at 1 atm. pressure. The desulfurization of all Fe-S alloys proceeds with increasing time, the result of which is in accordance with that of W.A. Fischer and A. Hoffmann[6]. The slight increase of sulfur content observed in the previous work[1] was not obtained in the present case.

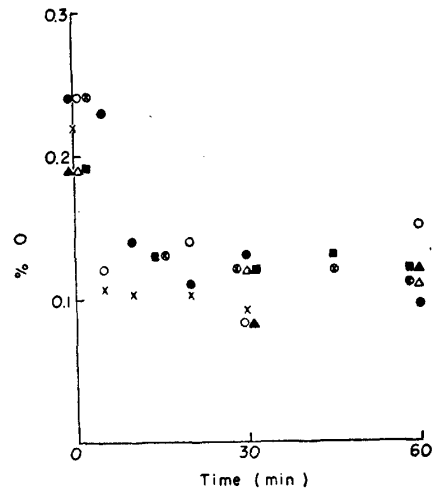
Oxygen analysis was made by the inert gas fusion method as well as by the vacuum fusion method. H.L. Hamner and R.M. Fowler[7] have reported that according to the vacuum fusion method, the analytical value of oxygen in specimens with high sulfur is higher than the actual content. Therefore, to eliminate carbon disulfide which was considered to affect the analytical value of oxygen, a trap cooled by dry ice was applied to the inert gas fusion method. However, in the vacuum fusion analysis the formation of COS besides CS_2 has been confirmed[7] and the effect of COS on the analytical value of oxygen is not obvious. Hence, a further investigation is required for the method of oxygen analysis in high sulfur alloys.

(2) M.N. Dastur and J. Chimpan, Trans. AIME, **185** (1949), 441.
(3) J.F. Elliot and M. Gleiser, *Thermochemistry for Steelmaking*, Vol. 1, Addison Wesley Publshing Co., Inc., (1960).
(4) T. Saito and Y. Kawai, Bull. Res. Inst. Min. Dress. Met., Tohoku University, **15** (1959), 103.
(5) L. Brewer and G.M. Rosenblatt, Trans. AIME, **224** (1962), 1268.
(6) W.A. Fischer und A. Hoffmann, Arch. Eisenhütt., **31** (1960), 411.
(7) H.L. Hamner and R.M. Fowler, Trans. AIME, **194** (1952), 1313.



Mark	Alloy No.	Crucible	Crucible Size (mm)	Amount
×	3609-3	Alumina	40×48×100	150g
⊗	6301-2	Alumina	40×48×120	150
○	3512-7	Alumina	40×48×100	100
●	3512-7	Magnesia	25×35×100	100
△	3512-6	Alumina	40×48×100	150
▲	3512-6	Magnesia	40×50×100	150
■	6301-1	Alumina	40×48×120	150
□	6210-5	Alumina	40×48×120	150

Fig. 1. Desulfurization of Fe-S alloys in vacuum melting at 1600°C.



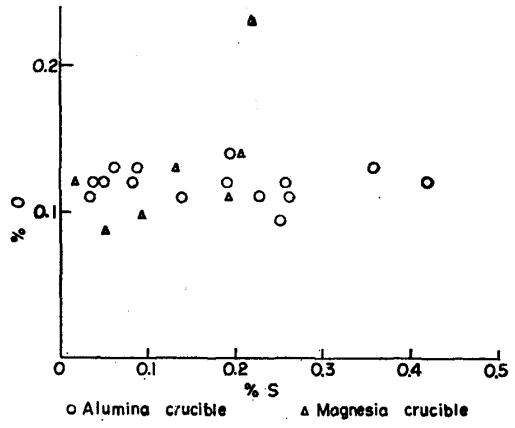


Fig. 2. Fig. 3.

Fig. 2. Relation between the oxygen content of Fe-S alloys and the time of vacuum melting.

Fig. 3. Sulfur and oxygen contents of Fe-S alloys melted in vacuum at 1600°C.

The results in Figs. 1 and 2 show that the desulfurization proceeds independently of the deoxidation. As shown in Fig. 3, no relation exists between the concentrations of S and O. Therefore, it is inferred from these results that the desulfurization proceeds not by the reaction

Table 2. Relation between the chemical composition in percentage of Fe-S alloys and the time of vacuum melting

Time (min)	Crucible	Alloy No.	C	Si	Al	Mg	N	H
—	—	3609-3	0.005	0.007	0.017	—	0.008	0.0027
5	Alumina	3609-3	0.005	0.005	0.008	—	0.006	0.0020
10	Alumina	3609-3	0.003	0.005	0.007	—	0.005	0.0017
20	Alumina	3609-3	0.003	0.006	0.009	—	0.005	0.0014
30	Alumina	3609-3	0.003	0.006	0.009	—	0.005	0.0011
60	Alumina	3609-3	—	0.007	—	—	—	0.0016
—	—	6301-2	0.006	0.009	0.003	—	0.010	—
15	Alumina	6301-2	0.005	0.005	0.003	—	0.007	—
30	Alumina	6301-2	0.005	0.005	0.003	—	0.006	—
45	Alumina	6301-2	0.008	0.007	0.003	—	0.006	—
60	Alumina	6301-2	0.001	0.005	0.002	—	0.006	—
—	—	3512-7	0.011	0.005	0.023	trace	0.008	0.0018
5	Magnesia	3512-7	—	0.009	—	trace	0.008	0.0049
10	Magnesia	3512-7	—	0.014	—	trace	0.008	0.0015
20	Magnesia	3512-7	0.005	0.009	—	trace	0.007	0.0027
30	Magnesia	3512-7	0.024	0.005	—	0.003	0.005	0.0040
60	Magnesia	3512-7	0.015	0.007	—	trace	0.006	0.0023
5	Alumina	3512-7	—	0.002	0.019	—	0.008	0.0018
20	Alumina	3512-7	0.007	0.002	0.018	—	—	0.0018
30	Alumina	3512-7	0.004	0.002	0.007	—	—	0.0014
60	Alumina	3512-7	0.008	0.002	0.008	—	—	0.0014
—	—	3512-6	0.003	0.009	0.007	—	0.007	0.0017
30	Alumina	3512-6	0.003	0.012	0.005	—	0.004	0.0009
60	Alumina	3512-6	0.003	0.009	0.004	—	0.004	0.0009
30	Magnesia	3512-6	0.004	0.009	—	trace	0.004	0.0009
60	Magnesia	3512-6	0.003	0.012	—	0.003	0.004	0.0009
—	—	6301-1	0.014	0.004	0.004	—	0.011	—
15	Alumina	6301-1	0.026	0.005	0.002	—	0.007	—
30	Alumina	6301-1	0.008	0.007	0.002	—	0.007	—
45	Alumina	6301-1	0.003	0.011	0.002	—	0.005	—
60	Alumina	6301-1	0.002	0.007	0.003	—	0.004	—

$$\underline{S} + 2\underline{O} = SO_2\,(g) \tag{5}$$

but by the reactions

$$\underline{S} = S\,(g) \tag{6}$$

and

$$\underline{S} = \frac{1}{2} S_2\,(g)\,, \tag{7}$$

and the deoxidation proceeds by the same reaction as that in the Fe-O alloy. This inference is approved by an experimental result in which Fe-S alloy (0.21 per cent S, 0.029 per cent C and 0.05 per cent O) deoxidized by carbon is desulfurized in the same rate as that in Fe-S alloy 3512–7 (0.24 per cent S and 0.24 per cent O) which was not deoxidized, while the deoxidation does not proceed.

As described in the previous report[1], although the desulfurization by the reaction (5) is expected from the standpoint of chemical equilibrium because the equilibrium partial pressure of SO_2 in the reaction (5) approximates to that of S or S_2 in the reaction (6) or (7), it may be considered that the experimental results do not

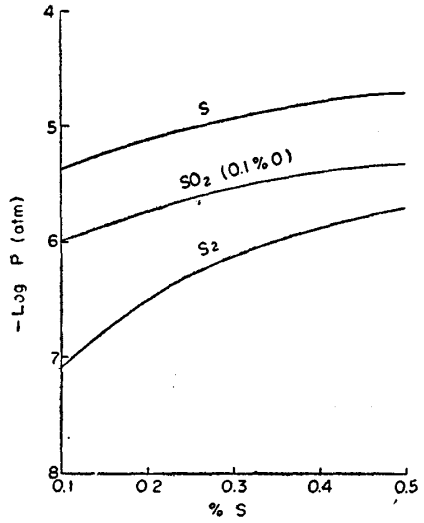


Fig. 4. Partial pressures of sulfur species and SO_2 vs sulfur percentage in Fe-S alloy at 1600°C.

Table 3. Thermodynamic data used.

Reaction	Standard free energy equation	Reference
$1/2\ O_2(g)=\underline{O}$	$\Delta F°=-\ 27{,}930-\ 0.57\ T$ cal	2
$\underline{S}=1/2\ S_2(g)$	$\Delta F°=+\ 28{,}180-\ 3.44\ T$ cal	9
$\underline{S}=S(g)$	$\Delta F°=+\ 71{,}430-18.04\ T$ cal	8, 9
$Si(l)+O_2(g)=SiO_2(s)$	$\Delta F°=-217{,}570+48.79\ T$ cal	16
$Si(l)+1/2\ O_2(g)=SiO(g)$	$\Delta F°=-\ 37{,}500-10.4\ T$ cal	17
$SiO_2(S)=\underline{Si}+2\underline{O}$	$\Delta F°=+146{,}500-56.3\ T$ cal	15

$\underline{S}$, $\underline{Si}$ and $\underline{O}$ denote infinitely dilute solution of sulfur, silcon and oxygen in pure iron respectively.

show the desulfurization by the reaction (5). The equilibrium partial pressures of SO_2, S and S_2 are shown in Fig. 4. Standard free energy changes in the reactions (6) and (7) are shown in Table 3. The activity coefficient of sulfur $f_{\underline{s}}$, and the equilibrium constant of the reaction (5) used for the calculation are as follows:

$$\log f_{\underline{s}} = -\ 0.028 \times [\%\ S]^{(9)}$$

and

$$K = \frac{P_{SO_2}}{f_{\underline{s}}\,[\%\ S]\cdot[\%\ O]^2} = 1 \times 10^{-3\,(10)}$$

respectively.

In addition to the desulfurization by the vaporization of sulfur, as a desulfurization reaction, W.A. Fischer and A. Hoffmann[6] have pointed out the following reaction between sulfur dissolved in iron melt and oxides constituting the crucible:

(8) G.R. St. Pierre and J. Chipman, JACS, **76** (1954), 4787.
(9) J.A. Cordier and J. Chipman, Trans. AIME, **203** (1955), 905.
(10) AIME, *Basic Open Hearth Steelmaking*, (1951), 681.

$$\underline{S} + MeO = MeS + \underline{O} \tag{8}$$

For simplification, however, on the assumption that desulfurization proceeds only by the reaction (6) by which atomic sulfur S having the highest equilibrium vapor pressure is formed, the following examinations were made of the rate of desulfurization.

(i) Assuming that the rate of vaporization of S at the surface of iron melt is a rate-limiting factor, the following equation[4] derived from Langmuir's equation may be applied:

$$-\frac{d[\%\,S]}{dt} = \frac{100A}{\rho V} \cdot \frac{\sqrt{M_s}}{\sqrt{2\pi RT}} P_s, \tag{9}$$

where A is the evaporation area, V the volume of iron melt, ρ the density of iron melt, M_s the atomic weight of sulfur, R the gas constant, 8.3×10^7 ergs/°c/mole, T the temperature in °K, and P_s the equilibrium partial pressure of S in the reaction (6). P_s is expressed by the equation[1]

$$\begin{aligned} P_S &= 4.07 \times 10^{-5} \times [\%\,S]\ \text{atm.} \\ &= 4.12 \times 10 \times [\%\,S]\ \text{dynes/cm}^2, \end{aligned} \tag{10}$$

which is applicable to a dilute solution of sulfur. In Eq. (9), the condensation coefficient α was assumed to be unity and the vaporization of iron was neglected. By integrating, Eq. (9) becomes

$$2.3 \log \frac{[\%\,S]_0}{[\%\,S]} = \frac{100A}{\rho V} \cdot \frac{\sqrt{M_s}}{\sqrt{2\pi RT}} kt, \tag{11}$$

where $[\%\,S_0]$ is the initial sulfur content, k the constant 4.12×10 and t the time in second. As shown by broken curves in Fig. 1, the rate of desulfurization calculated by Eq. (11) is much higher than that obtained by experiment.

(ii) Assuming that the diffusion of sulfur through a boundary surface of iron melt is a rate-limiting step, the following equation[11] based upon Fick's first law may be applied:

$$-\frac{d[\%\,S]}{dt} = \frac{A}{V} \cdot \frac{D_S}{\delta_S} \{\%\,S\ (\text{bulk}) - \%\,S\ (\text{surface})\}, \tag{12}$$

where A is the boundary area, V the volume of iron melt, D_S the diffusion coefficient of sulfur and δ_S the effective thickness of diffusion boundary layer for sulfur. By integrating, Eq. (12) becomes

$$2.3 \log \left[\frac{\%\,S_0\ (\text{bulk}) - \%\,S\ (\text{surface})}{\%\,S\ (\text{bulk}) - \%\,S\ (\text{surface})} \right] = \frac{A \cdot D_S}{V \cdot \delta_S} \cdot t, \tag{13}$$

where t is the time in second and $\%\,S_0$ (bulk) the initial bulk sulfur content. % S

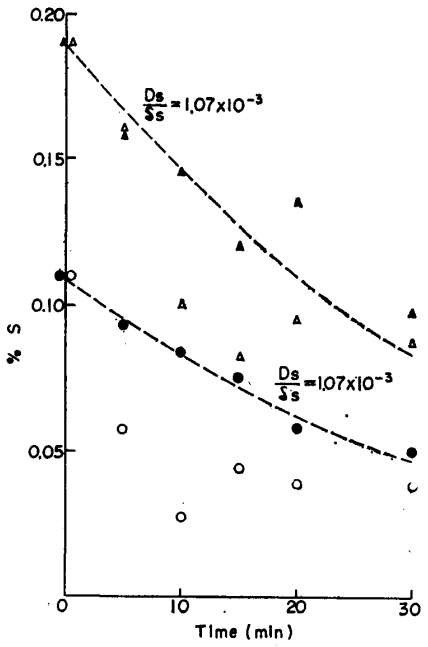
(11) T.B. King, Thermodynamics and Kinetics in Vacuum Metallurgy, in *Vacuum Metallurgy*, (1958), R. Bunshaw, Ed.

(surface) is obtained by taking P_S to be $10^{-3}/760$ atm. in Eq. (10).

As shown by solid curves in Fig. 1, Eq. (13) may explain the experimental results if D_S/δ_S is taken to be of the order of 10^{-3} to 10^{-4} cm/sec. However, when D_S is 1×10^{-4} cm^2/sec[12], δ_S becomes much larger than the film thickness for oxygen (0.003 cm)[13] which is postulated for the explanation of the rate of carbon drop in an open hearth.

3. Carbon-saturated Fe-C-S system

Experimental results are shown in Fig. 5. The graphite crucibles were used. Melting amount was 100 g. Vacuum melting was made after heating to 1600°C in argon at 1 atm. pressure. During vacuum melting a film was observed on the surface of melts and so the true temperature of the melt became uncertain. As can be seen in Fig. 5, two kinds of process are obtained. One is explained by Eq. (13) if D_S/δ_S is taken to be 1.07×10^{-3} cm/sec, and the other does not show the tendency of desulfurization after rapid desulfurization for initial $10\sim15$ minutes. The latter case has been previously reported[1]. Although the reason why the two kinds of process are obtained is not clear, the effect of the film on the temperature measurement or on the rate of desulfurization might account for it.



△▲ Original alloy 6210-3 (5.06%C and 0.045%Si)
○● Original alloy 6210-4 (5.01%C and 0.025%Si)

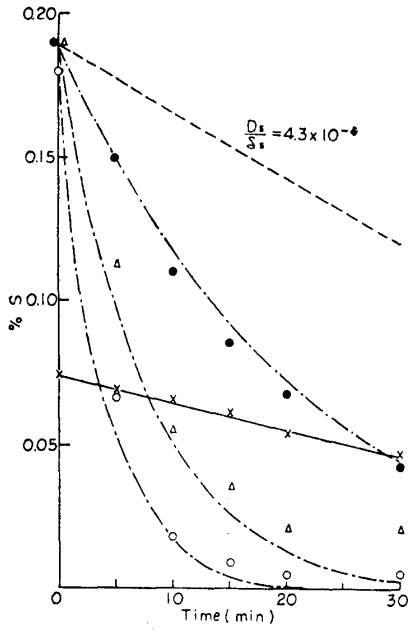
Fig. 5. Relation between the sulfur content of Fe-C-S alloys and the time of vacuum melting.

(12) AIME, *Basic Open Hearth Steelmaking*, (1951), 610.
(13) AIME, *Basic Open Hearth Steelmaking*, (1951), 613.

4. Fe-Si-S system

(i) Desulfurization

Experimental results are shown in Fig. 6. Vacuum melting was made after heating to 1600°C in argon at 1 atm. pressure. One hundred and fifty grams of Fe-Si-S alloy was melted in the alumina crucible, 40 mm in internal diameter, 48 mm in external diameter and 120 mm in height. The chemical composition of alloys used is shown in Table 4. As described in the previous report[1], the higher the



○ 6211-6 △ 6211-7 ● 6211-8 × 6211-9

Fig. 6. Relation between the sulfur content of Fe-Si-S alloys and the time of vacuum melting.

Table 4. Chemical composition in percentage of Fe-Si-S alloys used.

Alloy No.	C	Si	S	O
6211-6	0.014	2.99	0.18	0.054
6211-7	0.009	2.04	0.19	0.050
6211-8	0.011	1.65	0.19	0.047
6211-9	0.008	0.42	0.074	0.043

silicon content is, the higher the rate of desulfurization becomes. The desulfurization rate of Fe-Si-S alloys containing high silicon is high, compared with that of Fe-S and Fe-C-S alloys. In view of the equilibrium partial pressure of desulfurization products, the desulfurization is considered to be made by the following reaction[1]:

$$\underline{Si} + \underline{S} = SiS\,(g) \qquad (14)$$

Recently this reaction has been examined by Y. Shiraishi and others[14].

During vacuum melting boiling was not observed. Therefore, the following interpretation was made of these experimental results. If D_S/δ_S is assumed to be 4.3×10^{-4}/cm/sec, the experimental result shown by the mark $\times$ can be explained by Eq. (13), while other experimental results, in which original Fe-Si-S alloys contain 0.19 per cent S, cannot be explained by Eq. (13) as shown by the broken curve in Fig. 6. In this case % S (surface) in Eq. (13) was taken to be zero. Since the desulfurization rate depends largely on silicon content, so far as D_s/δ_s is constant, these experimental results cannot be explained by Eq. (13). Therefore, it is assumed that the rate of desulfurization is expressed by the following equation:

$$-\frac{d\,[\%\,S]}{dt} = K \cdot P_{SiS}\,, \tag{15}$$

where K is a constant depending on alloy system and experimental condition, and P_{SiS} the equilibrium partial pressure of SiS in Eq. (14). As described in the previous report[1], P_{SiS} is expressed as follows:

$$P_{SiS} = C \cdot \%S\,,$$

where C is a constant depending on silicon content and calculated from standard free energy change in Eq. (14), the activity of silicon and the activity coefficient of sulfur in Fe-Si-S alloy. Therefore, Eq. (15) can be integrated as follows:

$$-\int_{\%S_0}^{\%S}\frac{d\,[\%\,S]}{[\%\,S]} = K \cdot C \cdot \int_0^t dt\,, \tag{16}$$

Hence,

$$2.3\log\frac{\%\,S_0}{\%\,S} = K \cdot C \cdot t\,, \tag{17}$$

where % S_0 is the initial sulfur content at t=0. When K is taken to be 2.3×10^{-2}, the experimental result shown by the mark $\times$ can be explained by Eq. (17). K is so chosen that the curves close to the experimental results can be drawn according to Eq. (17) as shown by chain-curves in Fig. 6. Although Langmuir's equation is of the same type as Eq. (15), the rate of desulfurization calculated by it ($\alpha=1$) is much higher than that obtained by this experiment.

(ii) Deoxidation

Experimental results are shown in Figs. 7 and 8. Oxygen was analysed by the innert gas fusion method. The marks in Fig. 7 correspond to those in Fig. 6. The oxygen contents at t=0 are those in equilibrium with SiO_2 and were calculated from the relation [% Si] [% O]^2=2.8×10^{-5} obtained by N.A. Gokcen and J. Chipman[15]. The circles in Fig. 8 show experimental results. The chain-curve

(14) Y. Shiraishi, T. Saito and Y. Kawai, Bull. Res. Inst. Min. Dress. Met., Tohoku University, **16** (1960), 127.

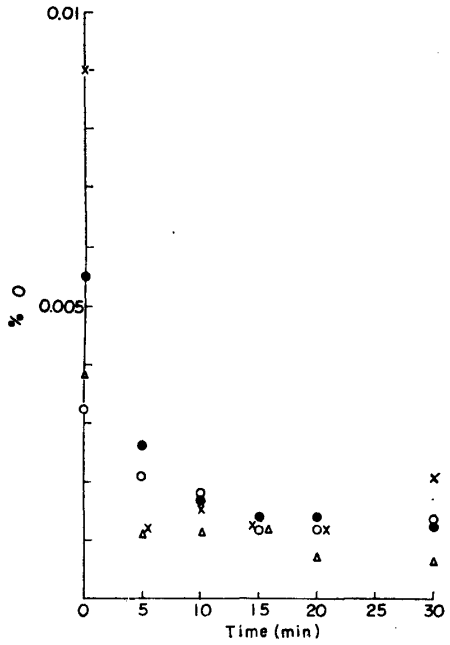


Fig.7.

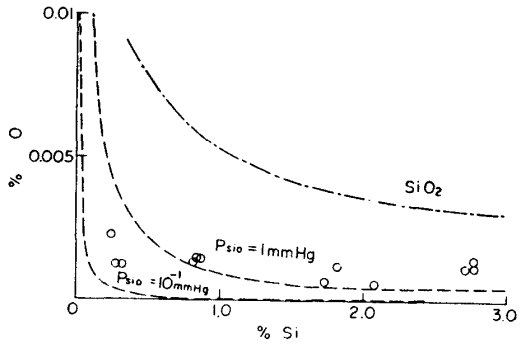


Fig. 8.

Fig. 7. Relation between the oxygen content of Fe-Si-S alloys and the time of vacuum melting at 1600°C.

Fig. 8. Relation between %Si and % O of Fe-Si-S alloys melted in vacuum at 1600°C for 15,20 and 30min.

shows the relation between % Si and % O in equilibrium with SiO_2 which was calculated from the above-mentioned relation[15], and the broken curves are the relations between % Si and % O in equilibrium with SiO at 1 and at 10^{-1} mmHg which is formed by the reaction:

$$\underline{\mathrm{Si}} + \underline{\mathrm{O}} = \mathrm{SiO\,(g)} \tag{18}$$

These relations were calculated from the equation

$$K = \frac{P_{\mathrm{SiO}}}{a_{\underline{\mathrm{Si}}} \cdot a_{\underline{\mathrm{O}}}} = 1.26\,, \tag{19}$$

where K is the equilibrium constant of the reaction (18), and $a_{\underline{\mathrm{Si}}}$ and $a_{\underline{\mathrm{O}}}$ are the activities of Si and O in Fe-Si alloy, respectively. K was calculated from the standard free energy change in the reaction (18), i.e.

$$\Delta F^\circ = 5{,}640 - 3.47\,T\,, \tag{20}$$

which was obtained from the standard free energy changes in the reactions shown in Table 3. The weight percentages of Si and O were used instead of a_{Si} and a_{O}. The oxygen contents obtained are lower than those in equilibrium with SiO_2 and close to those in equilibrium with SiO at 1 mm Hg. Because carbon contents are in the range of 0.001 to 0.005 per cent C which is the range of carbon content in electrolytic

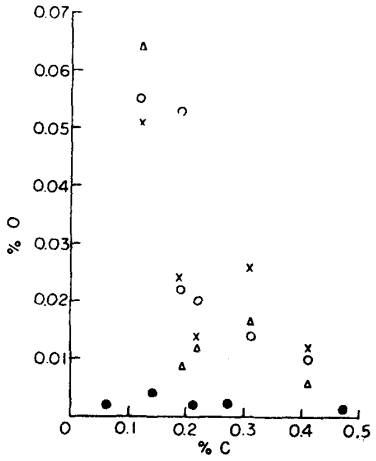
(15) N.A. Gokcen and J. Chipman, Trans. AIME, **194** (1952), 171.

iron, in view of the deoxidation in Fe-O alloy system, it may be inferred that the deoxidation proceeds according to the reaction (18). The possibility of deoxidation by the reaction (18) has been already pointed out by T. Saito and others[4]. T. Watanabe[18] has made an experiment with stainless steel, and considered that the deoxidation might occur by the formation of SiO.

5. Deoxidation of Fe-C and Fe-C-S alloys

Experimental results are shown in Fig. 9 and Table 5. Two hundred grams of each of Fe-C and Fe-C-S alloys was melted in alumina crucibles and then cast into the iron mold in argon at 1 atm. pressure. As shown in Fig. 9, the oxygen content of Fe-C-S alloys is higher than that of Fe-C alloys and shows a tendency of decrease with the increase of carbon content. The hydrogen content of Fe-C-S alloys is also higher than that of Fe-C alloys as shown in Table 5.

The following explanation was made of these results. For the deoxidation



Mark	Alloy	Analytical method
●	Fe-C	Vacuum fusion
×	Fe-C-S	Vacuum fusion
○	Fe-C-S	Inert gas fusion
△	Fe-C-S	Inert gas fusion

Fig. 9. Carbon and oxygen contents of Fe-C and Fe-C-S alloys melted in vacuum at 1600°C for 5 minutes.

Table 5. Chemical composition in percentage of Fe-C and Fe-C-S alloys melted in vacuum.

Alloy	C	H	S	Si	Al
Fe-C	0.063	0.00011	0.010	0.023	0.064
Fe-C	0.14	0.00019	0.012	0.045	0.029
Fe-C	0.21	0.00019	0.015	0.058	0.050
Fe-C	0.27	0.00006	0.014	0.039	0.063
Fe-C	0.47	0.00012	0.009	0.051	0.063
Fe-C-S	0.12	0.0011	0.39	0.014	0.010
Fe-C-S	0.19	0.0019	0.45	0.033	0.014
Fe-C-S	0.22	0.0006	0.44	0.040	0.024
Fe-C-S	0.31	0.0036	0.46	0.042	0.025
Fe-C-S	0.41	0.0012	0.44	0.058	0.037

(16) F.D. Richardson and J.H.E. Jeffes, J. Iron and Steel Inst., **160** (1948), 261.
(17) M. Gleiser, Trans. AIME, **221** (1961), 300.
(18) T. Watanabe, Tetsu to Hagané, **47** (1961), 1670.

reaction of molten iron with carbon

$$\underline{C} + x\,\underline{O} = CO_x\,(g) \tag{21}$$

the equilibrium constant K_C is given by

$$K_C = \frac{P_{CO_x}}{a_{\underline{C}} \cdot a_{\underline{O}}{}^x}, \tag{22}$$

where $a_{\underline{C}}$=activity of carbon

$a_{\underline{O}}$=activity of oxygen.

According to A.M. Samarin[19], in the process of interaction of carbon and oxygen in the molten metal, P_{CO_x} is expressed by the equation

$$\begin{aligned} P_{CO_x} &= P_1 + \rho h + \frac{2\sigma}{r} \\ &= K_C \cdot a_{\underline{C}} \cdot a^x{}_{\underline{O}} \\ &= K_C \cdot f_{\underline{C}} \cdot [\%\,C] \cdot f^x{}_{\underline{O}} \cdot [\%\,O]^x, \end{aligned} \tag{23}$$

where P_1=barometric pressure above the metal

ρ=molten metal density

h=depth of the metal at the level of gas bubble formation

σ=surface tension of molten metal

r=radius of a gas bubble

$f_{\underline{C}}$=activity coefficient of carbon

$f_{\underline{O}}$=activity coefficient of oxygen.

By the presence of sulfur the surface tension of liquid iron, σ, is strongly decreased. In carbon saturated Fe-C alloy at 1300°C, the addition of 0.4 per cent S reduces its σ (1650 dyne/cm) to about 900 dyne/cm[20]. Because carbon hardly affects the value of σ of iron, the reduction of σ may also be expected in a low carbon alloy. As can be seen from Eq. (23), when σ is effective on P_{CO_x} the reduction of σ by the addition of sulfur decreases P_{CO_x} value, and therefore, the reduction of oxygen is expected in contradiction to the experimental fact. Furthermore, according to the theory of nucleation, the nucleation rate of gas bubbles is increased by the lowering of σ, and the activity coefficients of carbon and oxygen are increased by the presence of sulfur.[21],[22] Therefore, according to these, the same may also be said of the effect of sulfur on oxygen content.

However, the following consideration may also be possible. The most probable sites of bubble formation are voids and cavities in the crucible wall[23] that

(19) A.M. Samarin, Deoxidation of Steel in Vacuum, in *Vacuum Metallurgy* (1958), R. Bunshaw, Ed.

(20) K. Monma and H. Sutô, Nippon Kinzoku Gakkai-Shi, **24** (1960), 611.

(21) E.T. Turkdogan, J. Iron Steel Inst., **182** (1956), 66.

(22) J. Chipman, J. Iron Steel Inst., **180** (1955), 97.

(23) L.S. Darken and R.W. Gurry, *Physical Chemistry of Metals*, McGraw-Hill Book Company, (1953), 491.

are not filled by the melt due to its inability of wetting the crucible. At such sites, the work of forming a bubble is minimum; hence, the rate of formation of bubbles is maximum[24]. When the surface tension of melt is lowered by the presence of sulfur, these voids and cavities will become filled by melt, and so, it may be concluded that the bubble formation of CO and H_2 etc. becomes difficult by the addition of sulfur. It may be said from the above-mentioned consideration that these experimental results show a stronger effect of crucible wall on degassing.

Summary

(1) In the case of Fe-O system, the alloy containing 0.2 per cent O was deoxidized to 0.1 per cent O and the alloy containing 0.06 per cent O was not deoxidized.

(2) In the case of Fe-S system, all the alloys containing 0.07 to 0.51 per cent S were desulfurized with increasing time. It was considered that the desulfurization and the deoxidation proceeded independently of each other. If D_S/δ_s is assumed to be of the order of 10^{-3} to 10^{-4} cm/sec, the rate of desulfurization can be approximately explained by an equation based upon Fick's first law.

(3) In the cases of carbon-saturated Fe-C-S alloys, two kinds of process were obtained. One was explained by the above-mentioned equation, and the other showed the rapid desulfurization at an early stage.

(4) In the cases of Fe-Si-S alloys, the rate of desulfurization can be explained by the equation which is of the same type as Langmuir's equation.

(5) In the cases of Fe-C and Fe-C-S alloys having the carbon content of steel, the oxygen contents of the Fe-C-S alloys containing about 0.4 per cent S were higher than those of the Fe-C alloys.

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(24) E.S. Machlin, Trans. AIME, **218** (1960), 314.